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Phenomenological Safety Studies on Sodium for CSP Applications

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Phenomenological Studies on Sodium for CSP Applications: A Safety Review

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Abstract

Sodium as a heat transfer fluid (HTF) can achieve temperatures above 700°C to improve power cycle performance for reducing large infrastructure costs of high-temperature systems. Current concentrating solar power (CSP) sensible HTF's (e.g. air, salts) have poor thermal conductivity, and thus low heat transfer capabilities, requiring a large receiver. The high thermal conductivity of sodium has demonstrated high heat transfer rates on dish and towers systems, which allow a reduction in receiver area by a factor of two to four, reducing re-radiation and convection losses and cost by a similar factor. Sodium produces saturated vapor at pressures suitable for transport starting at 600°C and reaches one atmosphere at 870°C, providing a wide range of suitable latent operating conditions that match proposed high temperature, isothermal input power cycles. This advantage could increase the receiver and system efficiency while lowering the cost of CSP tower systems. Although there are a number of desirable thermal performance advantages associated with sodium, its propensity to rapidly oxidize presents safety challenges. This investigation presents a literature review that captures historical operations/handling lessons for advanced sodium systems, and the current state-of-knowledge related to sodium combustion behavior. Technical and operational solutions addressing sodium safety and applications in CSP will be discussed, including unique safety hazards and advantages using latent sodium. Operation and maintenance experience from the nuclear industry with sensible and latent systems will also be discussed in the context of safety challenges and risk mitigation solutions.

ACKNOWLEDGMENTS

CONTENTS

FIGURES

TABLES

1. INTRODUCTION

1.1 Motivation for Latent Sodium in CSP Systems

Sodium as a viable HTF in receiver systems. Sodium is a promising option as a heat transfer fluid (HTF) for advanced high-temperature CSP receivers due to its high operating temperatures and thermal conductivity, which results in high heat-transfer coefficients and minimized heat-transfer surfaces. Sodium is relatively inexpensive and has a number of distinct advantages over oils and salts in CSP applications, such as: raising the maximum receiver temperature, increasing the maximum thermal flux of the receiver, lowering the operational pressure of the primary HTF loop and preventing solidification in the receiver piping (sodium solidification temperature: 97.79°C). Currently, advanced design research initiatives [1] are calling for CSP flux levels that approach values up to 200W/cm² and temperatures of 700-800°C. HTFs such as nitrate salt mixtures currently used in central receiver plants are capable of only achieving bulk temperatures of 565°C, which is not suited for higher-efficiency power cycles such as ultra-supercritical steam power cycles (~590-620°C) [2] or advanced power cycles under development (e.g. sCO$_2$ Brayton cycle, 700°C+) [3]. For receiver systems latent HTFs operate based on heat that causes a change of state but not a change in temperature, whereas sensible HTFs facilitates a change in temperature but not state. Previous sensible receiver systems using sodium as a HTF have demonstrated enhanced receiver efficiencies between 90-96% ±10% [4] at power levels up to 2.85 MW$_t$, as well as systems with thermal efficiencies as high as 76% based on daily energy averages [5]. For sensible sodium systems, it has been shown [1] that external receiver systems perform significantly better than cavity receivers due to reduced convection losses and improved heat distributions [6]. Receivers with latent sodium for dish-Stirling systems [7] have demonstrated evaporation operating temperatures between 700°C-850°C. For a dish-Stirling engine with a heat pipe containing latent sodium, the cavity receiver efficiency was found to be as high as 93% for a peak absorber surface temperature of 830 °C [8], and a 20% system performance improvement was realized over the same system with a directly illuminated tubular receiver. While sodium is in a saturated state, temperatures within a receiver can remain uniform, which has benefits for minimizing thermal stresses by reducing front-to-back and areal tube temperature differences [3]. Latent sodium systems also match isothermal operation requirements for many thermodynamic cycles including Stirling engines [2]. To achieve these high operating conditions, sodium and other high-temperature metals [9] have high thermal conductivities that improve heat transfer and allow a receiver to operate at high heat flux levels, while maintaining an acceptable temperature difference between the absorber inner surface and the bulk fluid. Another advantage using sodium is its high heat capacity, which provides thermal inertia against overheating. Latent sodium, being electrically conductive, can also be pumped by electromagnetic pumps, thereby reducing the need for mechanical systems susceptible to operational mechanical fatigue. Sodium also does not need to be pressurized since its boiling point is generally higher than the receiver system's operating temperature. It does not easily corrode steel or nickel-based system parts if O$_2$ is properly controlled.

Latent sodium can be used to not only achieve higher solar receiver efficiencies, but can also reduce fatigue and failure hazards found with sensible sodium systems. Sodium vapor may be generated through boiling or evaporation from a porous wick structure, as in a heat pipe. Although sodium pool boiling has been studied extensively in both CSP and nuclear applications [3], forced convection boiling in tubes has been studied far less, and has improved safety

potential principally due to a lower latent transport pumped mass of sodium, which is a fraction of that in a sensible system. Latent systems exhibit lower pressures than pumped sensible systems, where at 800°C system pressures are half an atmosphere and most failures result in air ingress rather than sodium egress. However if tower-scale systems are employed, sodium vapor travelling to the ground level will likely experience pressures greater than 1 atm. Coupling a phase change storage material within a sodium-receiver system, will also reduce the risk for sodium and water coming into contact. Latent sodium under a low oxygen state is also compatible with many structural materials and does not have corrosion issues found with sensible sodium and other high-temperature HTF's, including molten salts. Thermodynamically, latent sodium receiver systems have potential for having an enhanced exergetic fit to high temperature CSP systems as shown by Fig. 1, which was developed by Andraka *et al.* for a dish Stirling system [8]. The investigators demonstrated that latent HTF CSP engines have significantly reduced exergy losses compared to sensible systems, when combined with a latent storage system. A similar near-isothermal supply of heat to the thermodynamic cycle is required for cycles such as a supercritical CO_2 (sCO_2) Brayton engine with one or more stages of reheat.
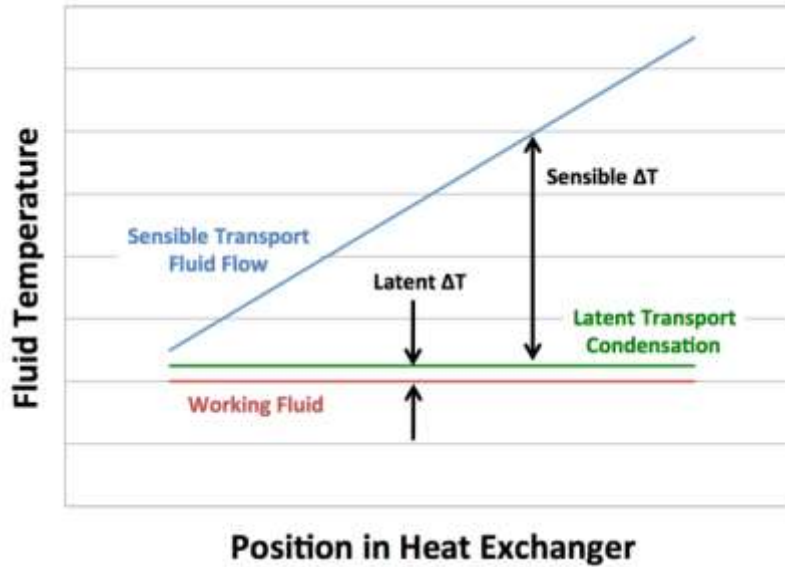
FIGURE 1. Comparison of sensible and latent heat transport into a Stirling engine [10].

Sodium and storage. It has previously been demonstrated [10] that thermal energy storage (TES) systems that employ a latent phase change material (PCM) can maximize the storage of useful energy (exergy) and at the system level, increase the efficiency of a power system [11]. Most thermal energy storage systems in operation are sensible; however storing heat in the form of latent heat of PCMs can significantly increase energy density [12]. Nithyanandam *et al.* [12] illustrated that the energy required to melt one kilogram of sodium nitrate by latent heating, is 75 times higher compared to the energy required to raise the temperature of one kilogram of the same substance by 1 K through sensible heating. Thus TES systems using latent sodium-based phase change materials have the advantage of being volumetrically compact in size with enhanced heat transfer coefficients. Thermodynamically, sensible systems have been shown to be a poor exergetic fit for high temperature CSP systems, which include highly recuperated sCO_2, phase change storage, hybrid storage and chemical processing [10].

2. HISTORICAL SODIUM SAFTEY CONTEXT

Public safety is vitally important for ubiquitous acceptance of CSP at large megawatt scales. Fire and operational instabilities are dominant contributors to risk events for advanced sodium high-temperature power systems. In addition to CSP, sodium also has applications as a high temperature (sensible) working fluid within the nuclear power industry [29, 35]. Since liquid sodium is better than water at evacuating heat from a reactor core, its high boiling point of $882^{o}C$ allows nuclear fast breeder reactors to operate close to atmospheric pressure, negating the need for thick steel containment vessels in pressurized water reactors [13]. Fast breeder reactors all over the world use liquid sodium as a coolant where there has been experimental and analytical research performed related to sodium fires as early as the 1950's [14]. Early research included droplet combustion, pool burning, suppression and large-scale sodium fire experiments. However, gaps still remain in our understanding of basic combustion behavior and combustion mechanics due to complexities of metal fire behavior. These gaps have led to little progress in understanding the basic combustion behaviors of sodium [15], where these concerns were noted as far back as 1972 [16]. Although new technologies and fire computational modelling capabilities [14] have substantially improved, most previous experimental investigations cannot be used to support models for today's systems. Clear definition of the experimental boundary and initial conditions are necessary to create current modeled system conditions. According to Makino et al. [15] reports of precise conditions in experiments are rare in the literature so heat transfer evaluations of sodium for today's systems have been almost impossible [14].

To date, only two fires have been reported with sodium as a HTF in CSP applications. These include incidents at Plataforma Solar de Almeria (PSA) in 1986 and at Vast Solar Jemalong in 2015. For PSA, despite engineering-designed best practices, failures to follow established procedures facilitated the sodium fire during maintenance [9]. A key reason for the incident was the decision by operators to carry out maintenance with pressurized storage tanks [17]. Many of the procedural recommendations from the accident (i.e. hazard analysis and maintenance) are now standard practice for CSP facilities involving potentially hazardous sodium processes [9]. One such recommendation came from receiver panels that required cover gas venting prior to the start of normal operation, which was found to be cumbersome and time-consuming, and led draining and re-filling to be infrequent. Other issues were found related to insufficient trace heating which resulted in sodium plugs that developed particularly around critical components. With regard to the Vast Solar Jemalong fire, all procedures were followed, and despite significant smoke, no injuries and no lasting significant damage occurred to the facility. All procedures were followed and proved sufficient for personnel and asset protection. From both cases, lessons learned can be applied to future system design to ensure safe, reliable operation.

In an IEA study [18], the Small Solar Power Systems (SSPS) project found that continual application of a Pyromark coating to piping walls facilitated uneven thickness distributions and conduction losses to the bulk sodium fluid which contributed to higher surface temperatures, stress and fatigue. Incidents with sodium have also taken place within the nuclear power industry, where fires were due to instrumentation and equipment failures (thermocouple [19], heating system [20], pressure regulation valve [20]) and human error [21]. System integrity issues have also been found due to thermal-mechanical piping fatigue and other reliability issues, which have resulted in ruptures that led to fires [20]. This work will provide a detailed assessment of adequate procedures and redundant system monitoring, minimizing the probability and magnitude of sodium leaks and fires.

3. SODIUM REACTIVITY & COMBUSTION

Sodium reacts with air and is inherently a potent reducing reagent and reacts violently with water to form hydrogen, then sodium hydroxide, and eventually sodium bicarbonate, depending on reaction conditions. It normally has an oxidation state of +1, and its single valence electron is lost with great ease, yielding a colorless sodium ion, Na^+. It reacts violently with mineral acids, halogens, and reacts exothermically with oxidizing agents, organic and inorganic halides, and protic media [22]. Sodium also reacts to generate shock-sensitive products with sulfur oxides and phosphorous, and reacts with many metal oxides such as mercurous and lead oxides. Sodium dissolves in many other metals such as potassium with great evolution of heat. The reactivity of a sample of sodium is largely related to its surface area. Therefore, reactions involving solid pieces of sodium, especially with an oxide or hydroxide coating, may be slow and controlled, whereas reactions with high-surface area sodium dispersions and liquid sodium may be vigorous [13].

3.1 Reactivity with Liquid Water

Contact of sodium with water or chlorinated hydrocarbons causes a violent exothermic reaction and may cause detonation of the released hydrogen. Although sodium has a high chemical reactivity with water, the heat release rate and heat of combustion is lower compared to conventional hydrocarbon fuels[13]. However in contact with water sodium often ignites the hydrogen liberated. Pure sodium begins to absorb oxygen while liberating hydrogen appreciably at approximately 100°C [23], where the rate of absorption increases with temperature. The reaction between sodium and water can be divided into two half-reactions, where Eqn. 1 describes the loss of electrons from sodium atoms, and Eqn. 2 describes when water molecules gain those electrons.

$$2[Na \rightarrow Na^+ + e^-] \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

The balanced equation for this reaction can then be written as:

$$2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g) \tag{3}$$
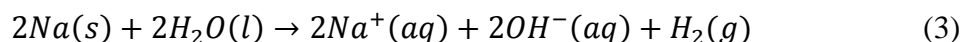
For the reaction of water with liquid sodium, the ease of surface area expansion can produce more explosive results since the reaction can be both highly exothermic and rapidly release hydrogen; where for a reaction at 25 °C, where sodium is a solid, approximately only 33.67 kilocalories per mole of heat is released [23]. However with high surface area contact with water the heat release is much more rapid. Additionally, secondary reactions accompany violent reactions with water, with the liberation of hydrogen gas which can be explosive when ignited by the exothermic reaction. The heat liberated in Eqn. 4, is sufficient to cause the reaction in Eqn. 5.

$$Na + H_2O \rightarrow NaOH + \frac{1}{2}H_2 + \dot{Q}_{Heat} \tag{4}$$

$$2H_2 + O_2 \rightarrow 2H_2O \tag{5}$$
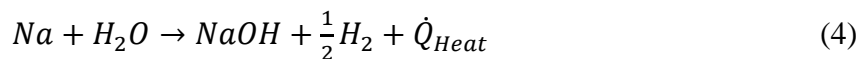
3.2 Reactivity with Air and Water Vapor

When exposed to air, sodium may ignite spontaneously at a temperature as low as 115 °C, depending on such conditions as humidity, dispersion, etc. For water vapor, sodium begins to absorb hydrogen appreciably at approximately 100 °C where the rate of absorption increases with temperature [23]. A sodium fire can be recognized by a very low flame with many bright yellow nodes. Sodium fires produce a dense white caustic smoke that contains highly alkaline material, sodium monoxide (Na_2O) and sodium hydroxide (NaOH), which can cause irritation and rapid tissue destruction through chemical and thermal burns. As the temperature increases above 650 °C, sodium can begin to spall concrete (which can cause secondary hazards such as flying debris), consume asbestos, firebrick, transite and other similar materials [13]. Under high pressure conditions, and temperatures above 300 °C, the formation of sodium peroxide is facilitated as the very reactive sodium material is consumed before each O_2 molecule can combine with enough sodium to form Na_2O, Eqn. 6.

$$2Na + O_2 \rightarrow Na_2O_2 \qquad\qquad (6)$$

Data on the combustion and burning rate of sodium in air and reduced oxygen atmospheres are required to predict the rate of energy release for a fire of a given size. Conversely, when sodium peroxide is dissolved in water, oxygen is evolved and an alkaline solution is then formed containing sodium hydroxide (Eqns. 7 and 8). Table 1 summarizes sodium fire tests conducted by various investigators [25-28] to determine approximate burning rates of sodium pools in air.

Peroxide: $$Na_2O_2 + H_2O \rightarrow 2NaOH + \frac{1}{2}O_2 + \dot{Q}_{Heat} \qquad\qquad (7)$$

Monoxide: $$Na_2O + H_2O \rightarrow 2NaOH + \dot{Q}_{Heat} \qquad\qquad (8)$$
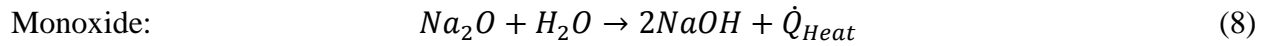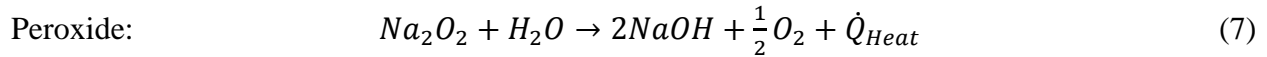
TABLE 1. Impacts of sodium combustion with air as provided by Griffin and Piccot [23].

Container Area [m²]	Air Flow Configuration	Container Depth [m]	Original Sodium Weight [kg]	Initial Sodium Temperature [°C]	Burning Time [hr]	Burning Rate [kg/hr/m²]	Reference
0.16	Natural	0.05	6.35	N/A	0.75	53.71	[25]
0.08	Natural	0.05	3.18	N/A	0.75	53.71	[25]
0.01	Natural	0.05	0.45	N/A	0.50	83.00	[25]
0.58	Natural	0.08	22.68	454	1.6	30.76	[26]
0.58	Forced	0.08	22.68	357	1.6	23.92	[26]
0.26	Natural	0.51	158.76	399	17	11.23	[27]
1.86	Natural	0.43	145.15	399	18	5.37	[27]
0.06	Forced	0.91	37.65	427	11	26.85	[28]
0.29	Forced	1.22	278.96	177	33	29.29	[28]

The quantities of sodium burned range from several grams to several hundred pounds, with large variability in pool size and initial sodium temperature. The data suggests that the initial sodium temperature above ignition is not an important variable for assessing average burning rate. It should be noted that the average burn rate was based on time required for complete combustion of sodium or an estimated fraction burned.

Table 2 presents data on the effect of water vapor on various modes of reaction between sodium and oxygen. The results suggest that for the range of moisture conditions evaluated, low moisture content is not a significant factor for a sodium fire; however temperature dependencies on combustion are evident especially for oxygen concentrations greater than 4%. For CSP systems however these temperatures are likely to be exceeded where combustion may also be possible.

TABLE 2. Effect of water vapor on sodium combustion as prescribed by Girffen and Piccot [23].

Oxygen content of gas		Ratio	Moisture Content [mm Hg]	Observations	Temperature of Sodium [°C]	Remarks
mm Hg	% at 1 atm					
900		5×10^5	0.00002	No Reaction	549	Range of O2 content of 10 to 900 mm Hg; maximum temperature employed.
900		9×10^3 to 4×10^5	0.0001 to 0.1	Ignition	110<ignition temperature<549	No reaction until ignition temperature was reached; above ignition temperature, vigorous combustion was observed.
900		$< 7 \times 10^3$	0.01 to 0.25	Slow reaction	104	Immediate reaction with no ignition of sodium
	6.5	~15	3	Burning	427	Appearance of burning nodules when oxygen concentration shown was reached.
	4.6	~10	3	Burning	538	Nodules on surface burning vigorously when oxygen content shown was reached.
	5.2	~0.3	140	Burning	538	

CSP applications can involve steam and sodium loops which can pose a hazard in the event of faulty piping, heat exchangers, pumps, etc. Although water and steam are principally identical with respect to chemical composition, steam does not however react with sodium as violently as with liquid water. In the presence of water vapor, sodium oxide aerosols react very rapidly to produce soda. Relative humidity (RH) influences product particle sizes, where sodium oxide particles released into a humid atmosphere absorb water until the vapor pressure above the formed sodium hydroxide solution is equal to the vapor pressure in the surrounding atmosphere [29]. Sodium hydroxide particles are always droplets above 35% relative humidity [29] though increase corrosive behavior for lower RH levels. This corrosion behavior can also be accelerated

by the presence of small levels of impurities in the sodium. The minimum temperature at which sodium will ignite with water vapor depends on the characteristics of the particular system involved. According to Griffen and Piccot [24] the ignition temperature is a function of such variables as the surface-mass ratio, surface conditions, metal purity, absolute humidity, ambient temperature and the velocity of air over the surface. The authors reported the effect of moisture content of the reacting atmosphere on sodium combustion and ignition.

During fires a CO_2-contianing atmosphere can arise which can transform sodium hydroxide particles/droplets into solid sodium carbonate particles, which can occur rapidly as a function of relative humidity. As illustrated by Jordan et al. [29], this conversion at 50% RH occurs 5 times faster than at RH levels less than 3% [29]. This may be explained that as the surface of wet particles are converted to solid crystal carbonate, a diffusion barrier may be formed, where smaller particles have a higher content of sodium carbonate than larger ones. As show in Fig. 2, after 260 seconds, only at higher RH levels above 50%, is 100% sodium carbonate realized [29], which would facilitate a safe environment after a fire considering all of the volatile sodium aerosols that had progressed fully through reaction.
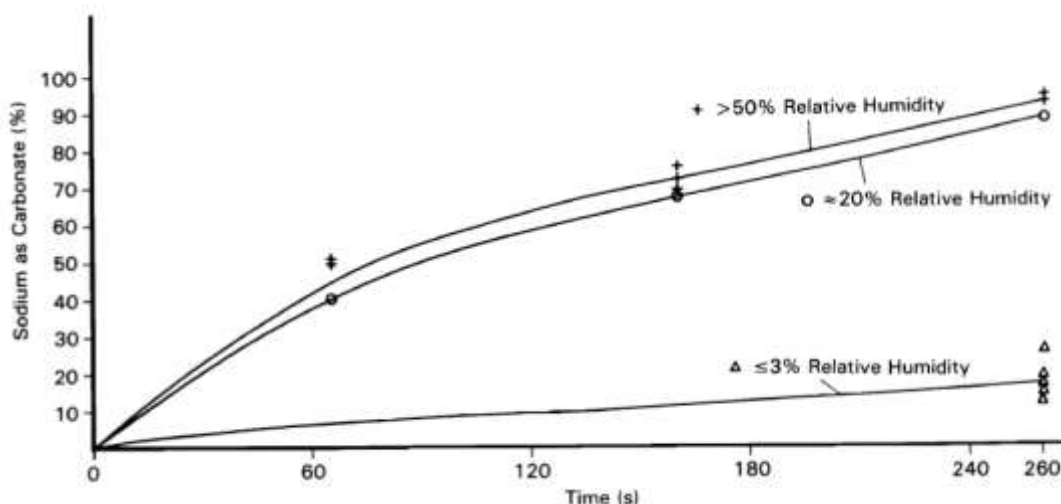
FIGURE 2. Formation of carbonate from sodium fires under varying relative humidity conditions [29].

4. SODIUM LEAKAGE, AEROSOLS AND COMBUSTION PRODUCTS

The consequences of sodium leakage depend on the oxygen availability in the location of the system break or containment. The release rate of the combustion products of sodium is a function of the oxygen concentration and the burn rate. As described by Griffin and Piccot [24] the release fraction of sodium oxide when nitrogen, containing 4 vol. % O_2, is swept across a 3ft^2 surface of liquid sodium at flow rates of approximately 100 cfm was approximately 60%, though the release fraction in air for the same conditions was only 20%. Therefore the burning rate is proportional to the oxygen concentration and decreases as the oxygen is consumed and air expands out during a fire, which could facilitate a hazardous breathing environment. If the outer containment atmosphere is not inert, a sodium fire can ensue with aerosol product formation. Several investigators have found [29] that sodium and aerosol droplet ejection velocities from

piping breaks are generally greater than 10 m/s, where they quickly impact surfaces and freeze on contact. A general approximation by investigators [29] is that the aerosol production rate is equal to the combustion rate, where combustion takes place directly in the atmosphere of containment. For further containment, sodium vapor and aerosol hazards can be reduced through the utility of sealed vapor traps located near high temperature sodium equipment [13]. The consequences of Sodium leakages differ according to the type of dispersion of the resulting jet:

1. **Pool Fires:** Sodium rapidly flows down to form a pool in the lowest part of a confined space.

2. **Spray Fires:** The leakage flow is dispersed into small droplets that obey the laws of ballistics and burn according to flow rate, the shape of the break, or the presence of other exhaust flow obstacles.

3. **Column Fire:** Due to the presence of leak jackets, the sodium will flow downward in the form of a column, generating droplets on a surface below the ruptured piping.

4. **Combined Fires:** Both Pool and Spray Fires are concurrent or occur in sequence with each other.

For a pool fire, there is general agreement that the mean value of the aerosol production rate from sodium combustion in a confined contaminant, such as in Nuclear containment vessels, is approximately 40% of the quantity of sodium burnt [30]. The energy released by the burning pool to the surrounding atmosphere can cause a slow increase in pressure. However, thermodynamically sodium, within the temperature range 450 °C-875 °C, is subatmospheric where pressure increases tend to be minimal. For CSP applications however, confined containment issues may not be an issue where systems tend to be located in outdoor, unconfined spaces. According to Griffin and Piccot [24] when a pool of liquid sodium burns in air, the combustion reaction is characterized by a very low flame region and dense clouds of white oxide smoke. Heat must be supplied to start the combustion reaction of sodium at low temperatures, however once it is started; enough heat is liberated to maintain the reaction and a temperature rise of the molten liquid.

For spray and combined fires, the initial radius of sodium droplets in an undisturbed jet depends on the geometry of the ejector break:

$$d_m = 1.15 \times 10^4 \frac{d}{Re} \tag{9}$$

where d_m is the median diameter of the sodium droplets, d is the diameter of the ejector break and Re is the Reynolds number of the fluid passing out of the break. Investigators [29] consider the combustion rate as a mass gasification rate, where Sodium evaporation is assessed based on the expression:

$$K = -\frac{d(2R)^2}{dt} \tag{10}$$

where 2R is the droplet diameter. For combined fires, transient combustion time becomes longer where the proportion of unburnt sodium increases.

For CSP structures open to the outside environment, ambient aerosol release during a fire can readily be determined from its concentration reached in a CSP sodium loop and from ventilation exhaust rates during forced ventilation. Without forced ventilation, the amount of released aerosol depends on the natural air flow circulation above a hot surface induced by a fire, where an unstable outside atmosphere can facilitate an increased hot air mass assertion over a stable atmosphere. Tests performed by Jordan et al. [29], on a 20 m chimney tower with a sodium pool fire developed at the base showed that in conditions without natural draft, only 7% of the original quantity of sodium was released to the ambient, whereas under natural draft conditions (e.g., openings at the base and top of the tower) the percentage of sodium released increased as high as 21%. This reduces the level of potentially volatile sodium left in a structure after a fire; however increased entrapment of sodium combustion products that remain in a structure, can increase with the geometry and volume of internal gratings and landings.

5. SOLUTIONS TO ADDRESS SODIUM SAFETY

Through implementation of handling and engineering controls [31], safe and optimal heat transfer performance of CSP receivers using sodium can be realized. Solutions to address safety can be broadly categorized according to prevention and extinguishment. Design controls of receiver piping, such as utility of high conduction metals and absorber coatings, [2] have been shown to reduce thermal stress, while design optimization [20] can be leveraged to reduce cycle fatigue from induced vibration, which occurs in the direction of sodium flow. Flow boiling instabilities may be abated through the addition of small amounts of heavy inert gas (e.g. Xenon or Argon) which provides pre-existing bubbles that can be inflated with minor superheat that consistently provides low superheat startup and more stable operation [2]. For the design of CSP systems the following sections outline good general engineering practices and controls for ensuring sodium safety and system reliability.

5.1 Piping and Pumps

Piping systems that facilitate sodium transport should employ all-welded connections, free-surface and electromagnetic pumps to ensure reliable operation [29]. Due to severe effects of potential reactions between latent sodium with air, water and structural materials, systems must be designed with a high safety margin to avoid rupture. This is particularly important where internal reactions with water are possible, such as sodium and water heat exchangers. Designs using double-jacketed and concentric piping with an intervening inert gas component have been demonstrated to ensure safe operation [32]. Reliability issues, such as piping corrosion that can lead to mechanical failures and ruptures can be reduced with a high-temperature bake-out process to remove contaminants [2]. Additionally, service pumps and piping systems must be designed to provide net positive suction head to avoid cavitation which can cause vibration and damage to the system [13]. The designed piping configuration must also provide complete drainage. For isolation during maintenance, smaller pipelines can provide a means to freeze sodium in a section of pipe. The frozen-sodium plug can then act as a positive means of shutoff to supplement closed valves [33]. Owing to its high heat transfer coefficient, the temperature of

piping and vessels tend to follow the temperature of liquid sodium very closely. Therefore, rapid temperature transients in latent sodium media can too cause thermal transients in the piping [13].

Venting and draining provisions can be used to reduce system pressures and loss of potential flammable material if leaks do occur, or if excessive internal pressures develop as a result of interactions. Additionally, potential sodium system rupture may require additional relief protection beyond that provided by normal venting or off-gas handling systems [29]. This can be particularly true for heat exchangers containing high-pressure steam and sodium. Rupture disks and/or relief valves can be used to reduce hazards. Additionally, Adler et al. [13] suggests that pressure-relief devices be placed in the cover-gas space rather than in the wetted portion of the system. In relief systems, design considerations should prevent backflow of air into sodium systems after the pressure-relief action has taken place. For most latent systems inert cover gas is typically not employed which therefore have high vacuum pressures at low temperatures, where mechanical relief valve systems may be impractical from a system integrity point of view. For these systems, burst disks may be preferred in such applications. In nuclear applications [13] spring-loaded relief devices have been proven reliable for this function, while check valves have also shown dependability as backup for control valves or rupture disks. A highly reliable and redundant control system is recommended to avoid inadvertent scrams or sudden thermal shocks to the system [13]. Overall, it is recommended to also have duplicated primary sensing instrumentation for monitoring temperature and leak detection of critical portions of the sodium system.

For sodium-water heat exchangers, water inleakage and sodium outleakage can require complex leak-detector systems, which have been proven effective in reducing sodium fires [38]. However, the hazards these exchangers pose can be eliminated through the use of latent sodium coupled with a PCM material. If isolation valves are used within the CSP sodium system, the system should be designed to ensure that no section is isolated without appropriate relief protection. Adequate mechanical ventilation should be provided to maintain a negative pressure within enclosures or areas containing sodium. Temperatures should also be maintained and controlled to prevent freezing, overheating of materials, or loss of fluidity in sodium lines.

Finally, issues have been found with austenitic systems which use heated wrapping or cladding that can result in high temperature gradients along piping systems [39], although preheating operations can reduce these gradients [13]. According to Alder et al. [13] one of the main considerations in preheating sodium system design to ensure safety and reliability is to preheat empty systems before they are filled with sodium since it can act as a distributor and this will ensure relatively uniform heating of the equipment.

5.2 Cover-Gas Systems

Since liquid metals are highly reactive with atmospheric components such as air, an inert cover gas is often used to fill system compartments and components. Normally, the cover-gas systems are operated at small positive pressures to ensure complete absence of air leakage into a system. Typically for sodium applications, helium, argon and nitrogen are the most acceptable [13]. Sodium systems must be absolutely leak tight in the regions containing liquid, and similarly the gas-containment envelope must also be leaktight. Typically, cover-gas pressures are kept low to minimize the possibility of outleakage, although higher pressures can be required to provide additional pump-suction pressure, and to provide a pressure differential between primary and

secondary systems. The cover-gas system may require initial purification which can be accomplished through a drying process [13]. Nuclear and CSP power systems generally are supplied with pressure-control devices to introduce cover gas into various parts of the system containing liquid sodium, where gas lines are protected from sodium frost by vapor traps [34] which reduces the possibility of plugged gas lines. In nuclear applications gas lines often must be connected to sodium systems at normally wetted locations (e.g. vents required on sodium piping or sodium-filled equipment). Freeze traps are also frequently used in these locations to prevent sodium from entering gas lines. The freeze traps permit gas passage during fill. Sodium that enters the trap freezes and plugs the trap, which prevents further flow of sodium into the gas lines. The thermal design of a freeze trap must ensure that the trap will freeze promptly during the fill process and will not melt inadvertently during normal operation. To minimize leakage for cover-gas systems, all-welded construction is utilized, in addition to bellows-seal valves and resilient seat valves [13]. Cover gas systems and filling operations will require considerable adaptation to be applicable to latent systems, since presence of a cover gas may block vapor transport of heat to the storage system or steam generator.

5.3 Sodium Purification

Pure sodium is relatively compatible with normal construction materials in traditional sodium heat transfer systems [33]. However, certain contaminants, notably oxygen even in trace quantities, can render the sodium active and present hazards [35]. Therefore, oxygen content should be kept low, and for operation above 500 ^{o}C, below 10 ppm [13]. Additionally, research data provided by Roweland et al. [36] indicated that an oxygen concentration increase from 12 to 50 ppm could result in a fourfold increase in corrosion. A sodium purification system can be used to remove impurities from the sodium in the heat-transfer system and control corrosion and problematic mass-transport phenomena. The presence of undesirable impurities can also be detected, which could otherwise cause reliability and performance issues. Carbon contamination can also cause issues as carbon transfer can occur from ferritic to austentic steels, from steel to refractory metals, and across single metal systems due to temperature gradients [37]. Overall, decarburization reduces the strength of steels, and carburization embrittles steel and refractory metals. This is of particular concern in thin metals sections such as cladding or bellows [40]. One solution for enhancing sodium purification is the employment of a cold trap. Sodium oxide, sodium hydride, and other miscellaneous contaminants become quite insoluble at temperatures approaching the melting point of sodium (97.72 ℃). Thus, when sodium passes through a cold zone, many of the damaging contaminants precipitate out, and their respective concentrations can be reduced to very low values [35]. However, in situations where cold traps cannot precipitate out enough oxide, an appropriately sized hot trap could be used instead. These devices are filled with zirconium foil and operate at elevated temperatures above 500 ^{o}C, which will react with oxygen and can potentially reduce O_2 content below 1 ppm [13]. Generally, latent systems cannot incorporate cold traps easily, and so purification techniques will need to be adapted.

5.4 High-Temperature Operation and Thermal Shock

The high heat-transfer capability, high heat capacities, and low viscosity of sodium result in unique thermal shock design challenges. Sharp changes in piping cross section must be avoided since rapid changes in hot sodium flow can cause high thermal stress in relatively thin sections of metal. These sudden changes can be serious, especially within intermediate heat exchangers pipe nozzles [13]. To compensate, nuclear applications have leveraged thermal-shock liners which are designed to absorb high temperature transients without significant damage [24]. Thermal shock can also occur during any sudden unbalancing of flow which would result in rapid temperature transients and high temperature differences and stress across piping. Thermal problems can also exist in the design of double-wall, or secondary containment, piping systems. Under thermal transient conditions, in the liquid-metal system, the temperature of the inner pipe can change very rapidly relative to the temperature of the outer pipe and this induce severe thermal stresses at the junctures between the two walls, unless adequate provision is made to absorb the subsequent stresses. If the outer and inner pipe walls are of different expansion coefficients, a continuous potential source of thermal stress and deformation can ensue. Here, expansion joints can be used on the outer, or secondary, containment wall to absorb the expansion, while special sliding supports inside the outer wall can support the inner piping [24]. Additional thermal stress can ensue during preheating of a double-walled piping system where heating of the outer wall can occur more rapidly compared to the inner wall. Heaters must therefore be accurately controlled to assure that the differential expansion between the two walls is not excessive during preheating. Latent systems can introduce extremely high thermal transients as the vapor front progresses through the system during initial startup. This can be reduced through trace heating. In addition, as the front progresses, sodium condenses on the cold side of the front, and the resulting liquid must have a path to a collection point.

5.5 Fire Mitigation, Containment & Extinguishment

To reduce fire hazards, a number of steps can be taken such as leak valude isolation within the system design. In the event of a liquid sodium fire however, the low heat release rate reduces the risk of fire propagation as it is less severe than other common combustible fuels. For example, the heat released from burning liquid sodium (per m^2) is about 10 times less than that of a kerosene fire [41]. However, during a fire, the temperature of burning sodium can increase rapidly to more than 800°C, which can be difficult to extinguish. In the presence of even a moderately dry atmosphere sodium burns quietly, producing a white caustic smoke which can pose health hazards [29]. An alkali-metal fire is generally extinguished by the removal of oxygen. One of the best methods of fire prevention is to maintain a low oxygen concentration in the atmosphere in areas where sodium piping is operated. Since no volatile combustibles are evolved from alkali-metal fires, there is no flame but merely a glowing mass of burning sodium. However, such approaches may be impractical in CSP systems. A sodium fire in itself is not particularly hazardous except for resulting air-borne concentrations [24]. The secondary reactions with other materials increase the hazard. For example, a sodium fire on a concrete floor will overheat, facilitating a rapid rise in temperature that can cause internal water molecules to reach their respective boiling point which can throw burning sodium over a wide area, thereby increasing the damage potential far beyond the original fire region [24]. Firefighting and rescue

work under such conditions can therefore be quite hazardous, therefore provision of metal pans or vault lining to confine possible sodium spills reduces the hazard and permits effective firefighting [24]. Due to potential large quantities of evolved caustic smoke from sodium fires, respiratory protection is therefore required.

Hot sodium combines chemically with common fire-extinguishing agents such as carbon dioxide, carbon-tetrachloride, and dry-chemical-foams and can cause explosions and fire [17] Generally, sodium reactions with carbon dioxide produce not only highly caustic oxides such as Na_2O, but also poisonous carbon monoxide, CO. The formation and accumulation of CO in a confined environment can raise the possibility of asphyxiation. Sodium fires must be extinguished with a class D dry chemical extinguisher or by the use of several other types of fire-fighting materials provided by Table 3. Self-contained breathing apparatus is also required for fighting fires or for escape.

Additionally, reduction of trace amounts of humidity within the surrounding environment, as well as redundant design controls and vacuum systems, can reduce the onset and caustic hazards of sodium fires. Finally, to reduce the lasting impacts of a sodium fire, designs that facilitate natural draft within a tower can also be leveraged to reduce the level of potentially volatile sodium left in a structure after a fire. Research by Jordan et. al found this can be as high as 21% [29], where increased entrapment of sodium combustion products that remain in a structure after a fire, can increase with the topology and volume of internal gratings of service stairs and landings.

TABLE 3. Sodium and alkali-metal extinguishment materials

Material	Description
Soda Ash	This substance can be sprinkled, shovelled or sprayed from an extinguisher. The powder blankets the fire and tends to prevent reaction with the carrier gas or with the metal.
Zirconium Carbonate	This material is applied in the same fashion as soda ash and has been demonstrated [24] to be effective with sodium fires.
Powdered Graphite	This substance is an excellent blanketing agent with a two-fold advantage: 1) By blanketing the surface, the powder excludes air and suffocates the fire. 2) Since it is a good conductor of heat, the graphite can cool the burning metal help to extinguish the fire.
Met-L-X	When Met-L-X is sprayed or shovelled on a fire through an extinguisher device, it forms a crust that excludes oxygen from the fire and suppresses it. It is advisable [24] to intermittently sprinkle this substance on the burning surface to hasten the formation of the crust. Met-L-X is particularly suitable for sodium fires on walls and piping though after a fire is extinguished, all high-temperature equipment that was sprayed must be cleaned thoroughly to avoid corrosion.
Pyrene G-1 Powder	Graphite-based powder to be sprinkled onto a burning surface. Since it is not combustible, secondary fires will not result from it supplication.

White Silica Sand	This substance has been demonstrated effective and inexpensive for fighting sodium fires or damming flow to isolate a fire.
Ansul Purple K	Potassium bicarbonate substance that is a very good extinguisher for secondary materials in a sodium fire. Although it has no direct effect on burning alkali-metals, it is excellent on other materials such as burning wood and electrical insulation [24].
Calcium Carbonate	This substance works well on small leaks or fires when applied to gradually smother and prevent metal from flowing beyond the burning area.

5.6 Material Requirements

Materials selected for the system and respective environment should be compatible with sodium for all normal and abnormal conditions. The system designer should be fully aware of the many hazards associated with chemical incompatibility of sodium with several constituent CSP materials:

1. Construction Metals:
   Most iron and steel alloys are relatively inert and resistant to attack by liquid sodium and present no immediate safety hazards from chemical reactions [24]. However, not all alloys are suitable for systems at high-temperature and for long-lifetimes. Excessive corrosion or solubility can degrade system integrity and lead to hazardous conditions such as plugging, fouling, leaks and ruptures. Due to the low melting temperature of aluminum at approximately 660°C, it should not be expected to provide isolation or containment for sodium at high temperatures or during contingent situations. Other metals in addition to aluminum, such as tin, zinc, magnesium and copper have high solubility coefficients and should not be used in a system that will be in contact with latent sodium. Additionally, for high-temperature operation, nickel-based alloys such as Haynes and Inconel, can also be employed to provide strength and air-side-corrosion resistance.

2. Concrete:
   Spills of liquid sodium onto concrete may react with water or other inherent chemicals within the concrete and damage or destroy the surface. If a fire is allowed to burn for relatively long periods of time, a rapid rise in temperature occurs which can cause the internal water molecules to reach their respective boiling point that can facilitate spalling. This can also cause dispersal of hot sodium, caustic products, and concrete particles which can facilitate secondary fires. Proper engineering and administrative designs/controls should attempt to reduce the likelihood of liquid sodium exposed to concrete. Instead, it is suggested that drip pans or steel liners over concrete surfaces be used.

3. Insulating Materials:

Significant quantities of insulating materials can be required in any CSP application that handles liquid sodium, for systems, components and the facilities. If the materials are dry or do not contain chemically-bonded water molecules, the reactions do not present a direct hazard. The temperature of the sodium and the system should determine the selection of the most suitable insulation material. Some high temperature insulation materials may present respiratory issues after high temperature exposure, with hazards similar to asbestos. Safe alternatives can be employed, such as SB-silica blankets versus almunia-based blankets, are available and should be considered for systems that may be disturbed during maintenance functions.

6. CONCLUSIONS

Extensive experience using sodium as a HTF from CSP [31] and nuclear [29] applications position it as one of the most technologically ready candidates for high-temperature CSP receivers in terms of materials compatibility and operational safety issues [2], primarily through application of design and operational best practices. This investigation has found the utility of latent sodium, through reduced inventory and pressures, can also further reduce safety hazards while improving the reliability and performance of CSP heat exchange systems. Through implementation of handling precautions and engineering controls [31], safe and optimal heat transfer performance of heat exchangers using sodium as an HTF can be realized. Additionally, the use of latent sodium coupled with a PCM can be used to not only reduce hazards posed from sodium-water interactions, but also improve system costs and performance.

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